

*Dedicated to V.F. Mironov on His 60th Anniversary*

## Synthesis of Pillar[5]arenes with a PH-Containing Fragment

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**Abstract**—The reactions of phosphorus(III) chloride and 2-chloro-1,3,2-dioxaphospholane with monohydroxypillar[5]arene afforded for the first time the corresponding PH-phosphonates. It was found that the newly formed P–O(Ar) bond is characterized by considerably reduced reactivity, which was rationalized by essential shielding of the phosphorus atom by the pillar[5]arene macrocycle. The pillar[5]arene scaffold stabilizes the highly reactive  $P^{III}$ –Cl fragment, so that the formation of macrocyclic dichlorophosphite can be detected under normal conditions.

**Keywords:** phosphorylation, pillar[5]arene, PH-containing compounds, macrocycles

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The chemistry of macrocyclic compounds is the subject of extensive studies due to their tremendous importance and continuously extending scope of applications [1–3]. In the past few years, interest in the synthesis of these compounds has considerably grown because of their significance for the preparation of supramolecular materials [1–3]. For instance, many macrocycles have found application in such fields as chemical technology, metal separation, medicine, and ecology [4–8]. The design of synthetic macrocyclic receptors based on pillararenes, calixarenes, cyclodextrins, and resorcinarenes and capable of recognizing various substrates and promoting chemical transformations, is one of the vigorously developing lines of modern supramolecular chemistry [9–17]. Introduction of various organophosphorus fragments into macrocyclic structures enhances their coordination ability and gives rise to new types of supramolecular and organometallic coordination polymers with practically useful properties.

Herein, we describe synthetic approaches to pillar[5]arenes containing a PH-phosphonate fragment using phosphorus trichloride and 2-chloro-1,3,2-dioxaphospholane as phosphorylating agents. Initially, we have studied the reaction of monohydroxypillar[5]arene with 2-chloro-1,3,2-dioxaphospholane. The starting compounds, 2-chloro-1,3,2-dioxaphospholane [18] and

decamethoxypillar[5]arene (**1**) [19] were prepared previously according to known procedures (Scheme 1). Compound **1** was demethylated by the action of boron tribromide in anhydrous chloroform, and monohydroxy derivative **2** was purified by repeated washing of the precipitate with distilled water.

A widely used procedure for the synthesis of phosphorylated phenols involves fusion of the reactants. However, these conditions are inapplicable for macrocyclic compounds because of their high melting points. Therefore, the reaction was carried out in solution, and only two requirements were posed to the solvent [20–22]: boiling point in the range from 60 to 150°C and good solubility of the initial compound therein. It was shown previously that calixarenes react with 2-chloro-1,3,2-dioxaphospholane in *p*-bromotoluene or tetrahydrofuran [20–22]. Unfortunately, pillar[5]arene **2** is poorly soluble in these solvents, so that we first tried *p*-xylene. The reactants were heated under argon to 100°C (Scheme 2). After 12 h, the  $^{31}P$ –{ $^1H$ } NMR spectrum of the reaction mixture contained a signal of the phosphorylating agent and two other signals at  $\delta_P$  127.5 and 20.0 ppm which were assigned, respectively, to phosphite **3** and oxidation product of 2-chloro-1,3,2-dioxaphospholane, 2-chloro-1,3,2-dioxaphospholane 2-oxide (**4**).